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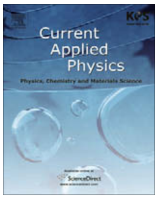

Growth, structural and optical properties of Cd$_x$Zn$_{1-x}$S thin films deposited using spray pyrolysis technique

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ABSTRACT

Cd$_x$Zn$_{(1-x)}$S (x = 0, 0.2, 0.4, 0.6, 0.8, and 1) thin films were deposited by the chemical spray pyrolysis technique using a less used combination of chemicals. Depositions were done at 573 K on cleaned glass substrates. The composition, surface morphology and structural properties of deposited films were studied using EDAX, SEM and X-ray diffraction technique. XRD studies reveal that all the films are crystalline with hexagonal (wurtzite) structure and inclusion of Cd into the structure of ZnS improved the crystallinity of the films. The value of lattice constant '*a*' and '*c*' have been observed to vary with composition from 0.382 to 0.415 nm and 0.625 to 0.6[illegible] nm, respectively. The band gap of the thin films varied from 3.32 to 2.41 eV as composition varied from x = 0.0–1.0. It was observed that presence of small amount of cadmium results in marked changes in the optical band gap of ZnS.

1. Introduction

Cd$_x$Zn$_{1-x}$S ternary compounds are promising materials for a variety of optoelectronic device applications, such as electroluminescent, photoluminescent and photoconductor devices [1–4] and especially in photovoltaic cells with different polycrystalline absorber materials like Cu$_x$[illegible] [5,6], CuInSe$_2$ [7,8], CdTe [9,10], CuGaSe$_2$ [11]. The reason is the possibility of tailoring its semiconductor properties between the values corresponding to the pure binaries. This fact allows to adapt the material properties to the device requirements. In recent years there have appeared several manuscripts on fabrication of these compounds by different methods such as physical vapour deposition (PVD) [12,13], chemical bath deposition (CBD) [14–20]. However only few manuscripts on preparation of Cd$_x$Zn$_{1-x}$S thin film by chemical spray pyrolysis [21,22] can be found, despite being one of the most common methods used for the deposition of II–VI compound semiconductor thin films.

The spray pyrolysis technique is particularly attractive because of its simplicity in comparison with methods requiring vacuum conditions or complex equipments. It is fast, inexpensive, vacuumless and is suitable for mass production. The spray pyrolysis technique is basically a chemical deposition technique, in which solutions of the desired material are sprayed onto a preheated substrate. Continuous films are formed onto hot substrate by thermal decomposition of the reactants. Films prepared by this technique are generally polycrystalline in structure and their properties are extremely influenced by the deposition process. In particular, spray pyrolysis has proved well suited for producing semiconductor films of the desired stoichiometry on large and non-planar areas. Although the spray deposition technique was employed earlier for the preparation of Cd$_x$Zn$_{1-x}$S thin films, cadmium chloride and zinc chloride were used as source for the cadmium and zinc in the deposits [21,22]. A summary of preparation of Cd$_x$Zn$_{1-x}$S thin films reported in the literature and corresponding sources of Cd, Zn and S is given in Table 1.

In this present work, cadmium acetate, zinc acetate and thiourea combination has been used as source materials for the first time (to the best of our knowledge) to fabricate thin films of Cd$_x$Zn$_{1-x}$S with different composition (x = 0.0–1.0) using spray pyrolysis technique. The growth, structural and optical properties of these films in relation to composition 'x' are reported and discussed.

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Table 1
A summary of preparation of $Cd_xZn_{1-x}S$ thin films reported in the literature and corresponding sources of Cd, Zn and S.

	Sources of Cd, Zn and S	Growth technique	$T_{deposition}$(°C)	Crystal structure	E_g (eV)	Reference
1.	CdS and ZnS powder	PVD	–	–	2.62–3.25	[12]
2.	CdS and ZnS powder	PVD	150	Wurtzite and zinc blende	2.39–3.53	[13]
3.	$CdSO_4$, $ZnSO_4$ and thiourea	CBD	70	Wurtzite	2.45–3.2	[14]
4.	CdI_2, ZnI_2 and thiourea	CBD	60–80	Wurtzite	2.5–3.6	[15]
5.	CdI_2, ZnI_2 and thiourea	CBD	80	Wurtzite	2.4–3.5	[16]
6.	$CdCl_2$, $ZnCl_2$ and thiourea	CBD	55	–	–	[17]
7.	$CdCl_2$, $ZnCl_2$ and thiourea	CBD	70	Wurtzite	2.34–3.43	[18]
8.	$CdCl_2$, $Zn(NO_3)_2$ and thiourea	CBD	80	Wurtzite	2.46–2.62	[19]
9.	$Cd(CH_3COO)_2$, $Zn(CH_3COO)_2$ and thiourea	CBD	75	Wurtzite	–	[20]
10	$CdCl_2$, $ZnCl_2$ and thiourea	Spray pyrolysis	275	Wurtzite	[illegible]	[21]
11.	$CdCl_2$, $ZnCl_2$ and thiourea	Spray pyrolysis	250	Wurtzite	2.486–3.[illegible]	[22]

2. Experimental details

$Cd_xZn_{1-x}S$ films of 1 µm thickness were deposited on glass substrates with different Cd concentrations (for $x = 0$, 0.2, 0.4, 0.6, 0.8 and 1) using chemical spray pyrolysis technique. Here x represents the Cd concentration in the spraying solution as also in the films. Aqueous solutions of 0.05 M $Cd(CH_3COO)_2{\cdot}2H_2O$, $Zn(CH_3COO)_2{\cdot}2H_2O$ and $CS(NH_2)_2$ were used as sources for Cd, Zn and S, respectively. Deionised water was used as a solvent. In each run, 100 ml of solution was sprayed at the rate of 2 ml/min on cleaned glass substrates maintained at an optimized temperature of 573 K. The thickness of the films was measured using optical and gravimetric methods. The films were characterized by X-ray diffraction (XRD) with Cu Kα radiation (Bruker axs D8 Advance model operating in Bragg-Brentano geometry) in the 2θ range from 20° to 60°. The surface properties of all the films were investigated using JEOL SEM 5800 LV. The compositions of samples were determined by energy dispersive X-ray spectroscopy (EDAX). The optical data were obtained within the spectral range 350–750 nm using UV–Vis spectrophotometer (GBC Cintra 101).

3. Results and discussion

3.1. Structural study

II–VI Chalcogenide semiconductor materials show the structural duality, and can be formed as either sphalerite (cubic) or wurtzite (hexagonal) type [23]. To determine the crystal structure of the $Cd_xZn_{1-x}S$ thin film, the X-ray diffraction patterns were studied. The XRD patterns of the $Cd_xZn_{1-x}S$ films are shown in Fig. 1a–f. The diffractograms indicate the presence of prominent peaks corresponding to (1 0 0), (0 0 2), (1 0 1) and (1 1 0) planes of the material with hexagonal [illegible] which were used for the calculation of lattice parameters. Moreover, the intensity of the (0 0 2) plane increased with the composition of cadmium, showing that the crystallinity of the films increased with 'x'. The standard crystallographic data for the CdS and ZnS metals were taken from JCPDS (card numbers 41-1049, 36-1450, respectively). In these entire compositions, the (0 0 2) diffraction peak was prominent. The plane (0 0 2) gives lattice matching to the chalcogenide semiconductor such as $CuIn_xGa_{1-x}Se_2$ and $CuIn(s_{1-x}Se_x)_2$, which are used in photovoltaic devices. For best solar cell efficiency, the composition of the $Cd_xZn_{1-x}S$ thin film must be in the range $x = 0.9$ to $x = 0.8$ [24].

The lattice constant a and c for hexagonal phase of CdZnS thin films are calculated using the following equation [25]

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}$$

The value of lattice constants 'a' and 'c' varies with composition from 0.382 to 0.415 nm (with a standard deviation of 0.005 nm) and 0.625 to 0.675 nm (with a standard deviation of 0.006 nm), respectively. Fig. 2 shows the variation of lattice parameters with the composition of cadmium from $x = 0$ [illegible]) in the films. It is observed that incorporation of Cd leads [illegible] an increase in the lattice parameter and hence the unit cell size. This is in agreement with the results obtained earlier [13,15,18]. The grain size 'D' of the samples was estimated by using 'Scherrer's formula [26].

$$D = \frac{0.94\lambda}{\beta \cos\theta}$$

where λ is the wavelength of the X-ray used, β is the broadening of the diffraction line measured at half of its maximum intensity (FWHM) and θ is the Bragg angle. The change in the values of lattice constant and the grain sizes with the composition x are given in Table 2. From this table it is observed that the grain size of the $Cd_xZn_{1-x}S$ films increases with increasing cadmium content, attains maximum grain size of about 12 nm for $x = 1$. It is concluded from the structural analysis that the Cd incorporation has a strong effect on the structural properties.

The composition of films was confirmed by energy dispersive X-ray spectroscopy (EDAX). Table 3 shows the composition of elements in film (with a standard deviation of 0.5% on an average for all the elements) and initial composition of elements in the sprayed solution. It is concluded that doping can be done very easily and effectively using spray pyrolysis technique. However, sulphur deficiency was observed in all the films. This may be due to the fact that sulphur has great affinity towards oxygen, so it might have converted to SO_2 and then evaporated.

Surface morphological study has been carried out on deposited films using scanning electron microscopy. Fig. 3 is a representative micrograph of ZnS film deposited onto glass substrate at a deposition temperature of 573 K. The film is observed to be uniform in thickness and composition, and is characteristic of deposits obtained by chemical deposition technique. The films with other chemical composition were also similar in their surface features.

3.2. Optical study

The absorption spectra of the $Cd_xZn_{1-x}S$ thin films for $x = 0.0$, 0.2, 0.4, 0.6, 0.8 and 1.0 were recorded in the wavelength range 350–750 nm. A representative plot of optical absorbance of film versus wavelength of light is shown in Fig. 4. The optical studies revealed that the films were highly absorptive with a direct type of transition, which allowed the optical band gap (E_g) to be determined using the following relationship

$$\alpha = \frac{A}{h\nu}(h\nu - E_g)^{\frac{1}{2}}$$

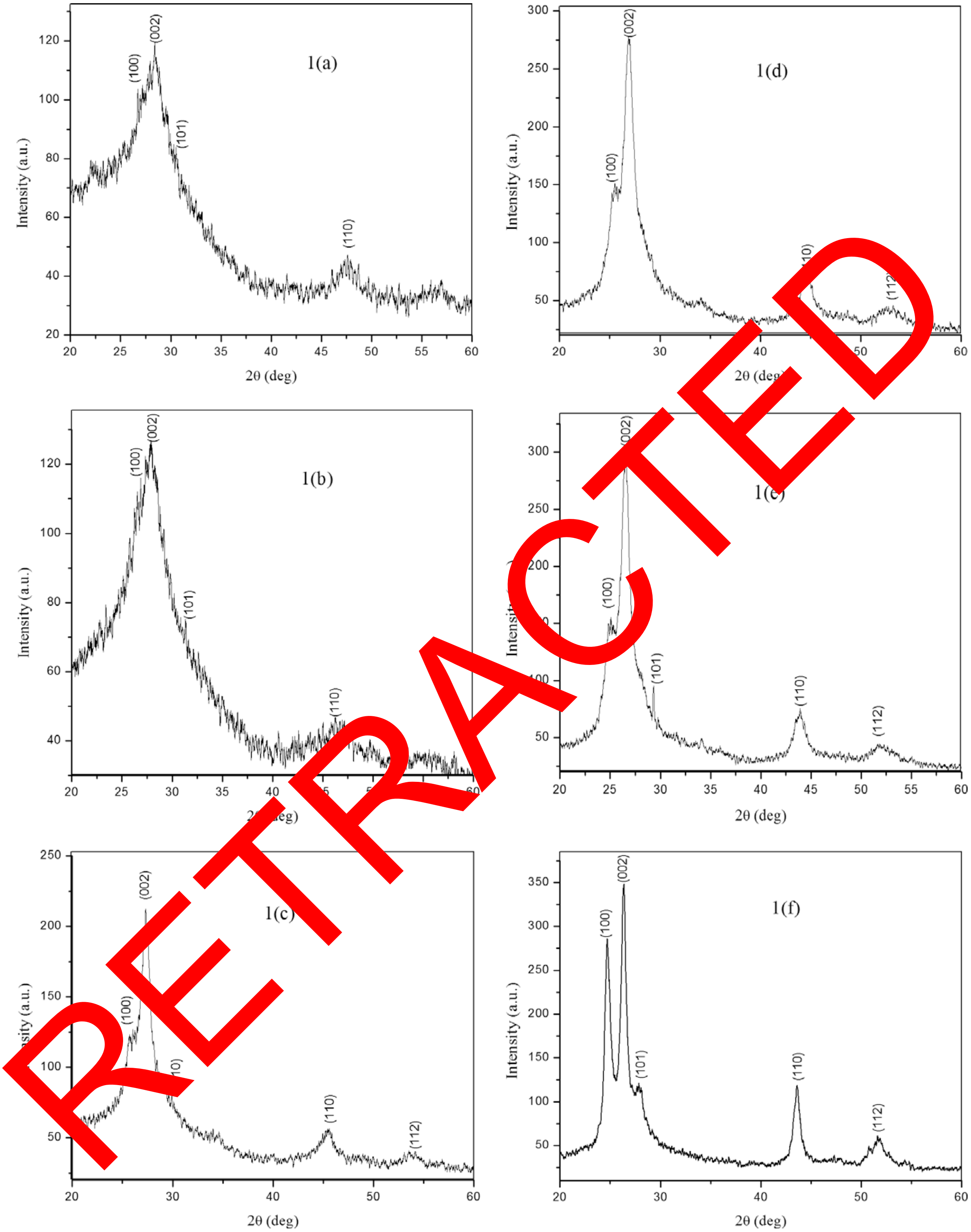

Fig. 1. (a–f) X-ray diffractograms of $Cd_xZn_{1-x}S$ films (a) $x = 0$, (b) $x = 0.2$, $x = 0.4$, (d) $x = 0.6$, (e) $x = 0.8$, (f) $x = 1$.

where '*A*' is a constant and '$h\nu$' is the radiation energy. The experimentally observed values of $(\alpha h\nu)^2$ plotted against $h\nu$ is shown in Fig. 5a–f for different composition. The linear nature of the plots at the absorption edge confirmed that $Cd_xZn_{1-x}S$ is a semiconductor with a direct band gap. The optical band gap is varied from 3.32 to 2.41 eV. The variation of band gap with the composition of x is shown in Table 2. It may be noted that absorption in the low energy region of the spectra arises due to fine grain structure of the films. Further, presence of steps or shoulders in the spectra indicates possible coexistence of additional phases. However, such variation in the composition across the samples was not detected by the chemical analysis using EDAX. It is observed that small amount of Cd

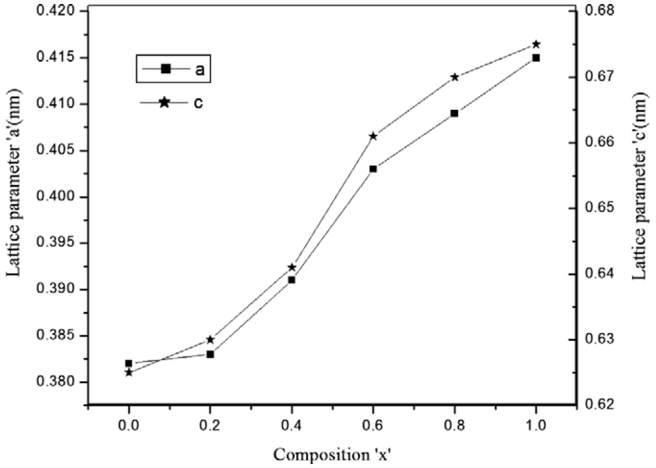

Fig. 2. Plot of lattice parameters versus Cd concentration (x).

present in the films greatly affects the optical band gap of ZnS. The band gap was observed to increase with an increase in the concentration of zinc in the deposits. The nature of this variation in the band gap energy may be useful to design a suitable window material in fabrication of solar cells.

4. Conclusion

$Cd_xZn_{1-x}S$ thin films have been synthesized for the first time by the chemical spray pyrolysis technique using aqueous solution of $Cd(CH_3COO)_2{\cdot}2H_2O$, $Zn(CH_3COO)_2{\cdot}2H_2O$ and CH_4N_2S. The XRD study showed the compounds to have hexagonal phase. It was observed that crystallinity of film increased with the composition. In the entire compositions, the (0 0 2) diffraction peak was prominent which gives lattice matching to the chalcogenide semiconductor such as $CuIn_xGa_{1-x}Se_2$ and $CuIn(S_{1-x}Se_x)_2$, which are used for photovoltaic devices. The lattice parameters are modified with the composition and optical band gap varies from 3.32 to 2.41 eV. It is easy to dope and get required composition and hence the optical band gap using spray pyrolysis technique. Presence of very small amount of cadmium greatly affects the band gap of ZnS films.

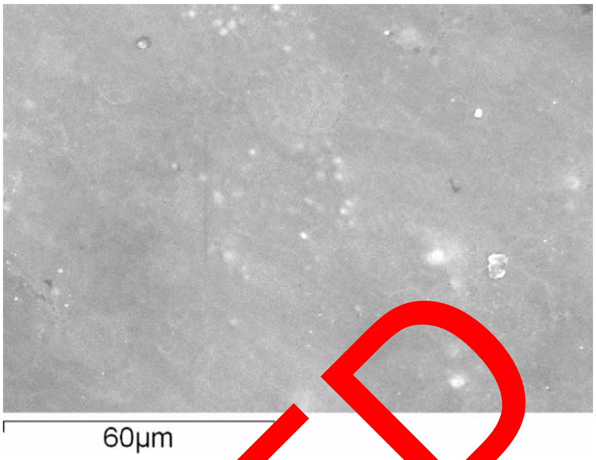

Fig. 3. A representative scanning electron micrograph of ZnS thin film.

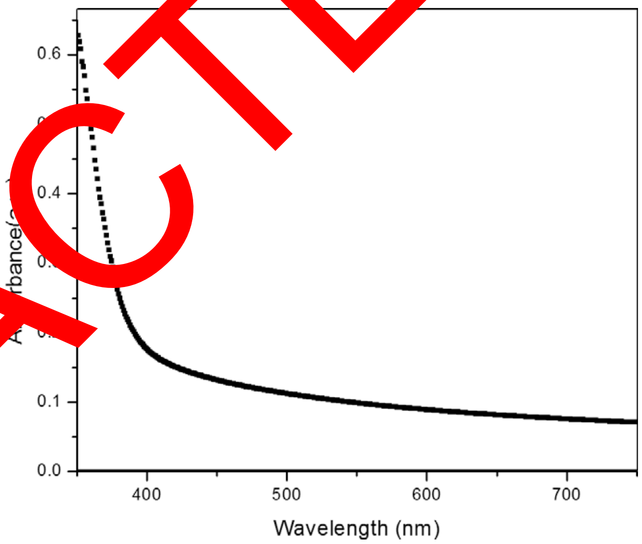

Fig. 4. A representative graph of absorbance versus wavelength of ZnS thin film.

Table 2
Summary of the structural parameters and band gap of $Cd_xZn_{1-x}S$ films.

Material	Lattice constants		Average grain size (nm)	Band gap (E_g in eV)
	a (nm)	c (nm)		
ZnS	0.382	0.625	4.5	3.32
$Cd_{0.2}Zn_{0.8}S$	0.383	0.630	5.1	2.98
$Cd_{0.4}Zn_{0.6}S$	0.391	0.641	7.0	2.83
$Cd_{0.6}Zn_{0.4}S$	0.403	0.661	8.3	2.70
$Cd_{0.8}Zn_{0.2}S$	0.409	0.670	9.5	2.55
CdS	0.415	0.675	12	2.41

Table 3
Elemental compositions of $Cd_xZn_{1-x}S$ thin film prepared by spray pyrolysis technique.

Composition 'x'	Film composition	Initial atomic percentage in the spray solution			Final atomic percentage in the film by EDAX analysis		
		Cd	Zn	S	Cd	Zn	S
0.0	$Cd_{0.0}Zn_{1.0}S$	00	50	50	00.00	51.84	48.16
0.2	$Cd_{0.2}Zn_{0.8}S$	10	40	50	10.44	40.81	48.75
0.4	$Cd_{0.4}Zn_{0.6}S$	20	30	50	21.44	30.46	48.10
0.6	$Cd_{0.6}Zn_{0.4}S$	30	20	50	31.63	20.59	47.79
0.8	$Cd_{0.8}Zn_{0.2}S$	40	10	50	41.5	10.36	48.14
1.0	$Cd_{1.0}Zn_{0.0}S$	50	00	50	51.91	00.00	48.09

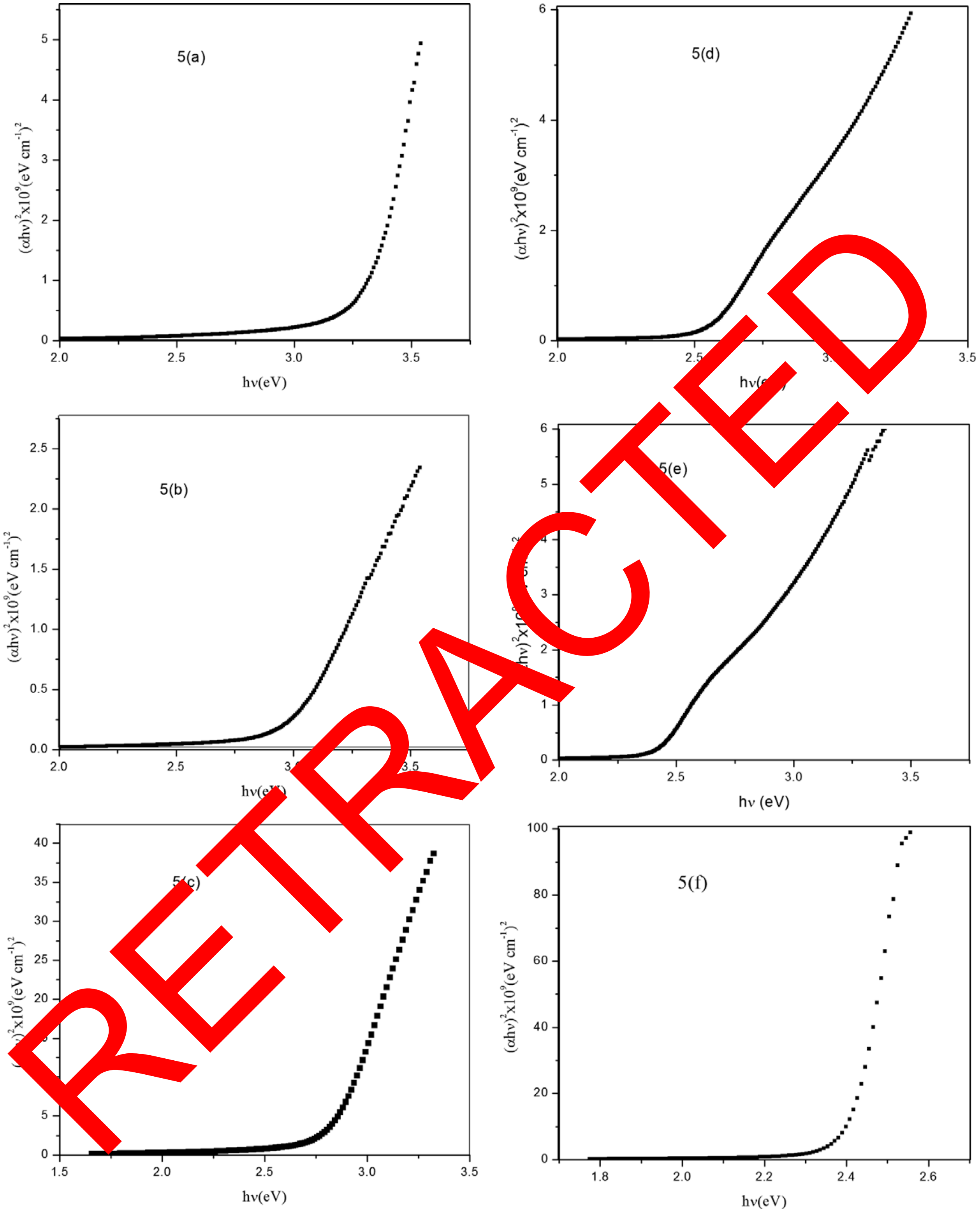

Fig. 5. (a–f) $(\alpha h\nu)^2$ versus $h\nu$ graphs of Cd_xZn_{1-x} S films (a) $x = 0$, (b) $x = 0.2$, (c) $x = 0.4$, (d) $x = 0.6$, (e) $x = 0.8$, (f) $x = 1$.

The range of band gap energy for the mixed films may be helpful in designing a suitable window material in fabrication of solar cells.

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References

[1] M.S. Abrahams, C.J. Buiocchi, J. Electrochem. Soc. 135 (6) (1988) 1578.

[2] J. Torres, G. Gordillo, Thin Solid Films 207 (1992) 231.
[3] G. Gordillo, Sol. Energy Mater. Sol. Cells 25 (1992) 41.
[4] J.M. Dona, J. Herrero, Thin Solid Films 268 (1995) 5.
[5] L.C. Burton, T.L. Hetch, Appl. Phys. Lett. 29 (1976) 612.
[6] H.L. Kwok, J. Phys. D: Appl. Phys. 16 (1983) 2367.
[7] R.R. Potter, J.R. Sites, Appl. Phys. Lett. 43 (9) (1983) 843.
[8] J.W. Bowron, S.D. Damaskinos, A.E. Dixon, Sol. cells 31 (1991) 159.
[9] O.M. Hussain, P.S. Reddy, B.S. Naidu, U. Uthanna, P.J. Reddy, Semicond. Sci. Technol. 6 (1991) 690.
[10] T.L. Chu, S.S. Chu, J. Britt, C. Feredikes, C.Q. Wu, J. Appl. Phys. 70 (5) (1991) 2688.
[11] K.T.R. Reddy, P.J. Reddy, J. Phys. D: Appl. Phys. 25 (1992) 1345.
[12] Pawan Kumar, Aparna Misra, D. Kumar, Neeraj Dhama, T.P. Sharma, P.N. Dixit, Opt. Mater. 27 (2004) 261.
[13] Jae-Hyoeng Lee, Woo-Chang Song, Jun-Sun Yi, Yeong-sik Yoo, Thin Solid Films 431–432 (2003) 349.
[14] J.M. Dona, J. Herrero, Thin Solid Films 268 (1995) 5–12.
[15] T. Yamaguchi, Y. Yamamoto, T. Tanaka, Y. Demizu, A. Yoshida, Thin Solid Films 281–282 (1996) 375.
[16] T. Yamaguchi, Y. Yamamoto, T. Tanaka, Y. Demizu, A. Yoshida, Thin Solid Films 343–344 (1999) 516.
[17] Isaiah O. Oladeji, Lee Chow, Thin Solid Films 474 (2005) 77.
[18] S.V. Borse, S.D. Chavhan, Ramphal Sharma, J. Alloy Compd. 436 (2007) 407.
[19] S.D. Chavhan, S. Senthilarasu, Soo-Hyoung Lee, Appl. Surf. Sci. 254 (2008) 4539.
[20] Jae-Hyoeng Lee, Woo-Chang Song, Jun-Sun Yi, Yeong-sik Yoo, Sol. Energy Mater. Sol. Cells 75 (2003) 227.
[21] Idris Akyuz, Salih Kose, Ferhunde Atay, Vildan Bilgin, Mater. Sci. Semicond. Proc. 10 (2007) 103.
[22] S. Ilican, M. Caglar, Y. Caglar, J. Optoelectron. Adv. Mater. 9 (2007) 1414.
[23] M. Bouroushian, Z. Loizos, N. Spyrellis, G. Maurin, Appl. Surf. Sci. 115 (1997) 103.
[24] S. Jiyon, S.S. Li, L. Chen, R. Noufi, T.J. Anderson, O.D. Crisalle, IEEE PVSC (2006) 534.
[25] Leonid V. Azaroff, Elements of X-ray Crystall[illegible]aphy, [illegible]raw-hill Company, Japan, 1968.
[26] A.R. Babar, P.R. Deshmukh, D. Haranath[illegible]H. Bhosale, K.Y. Ra[illegible]ure, J. Phys. D: Appl. Phys. 41 (2008) 135404.